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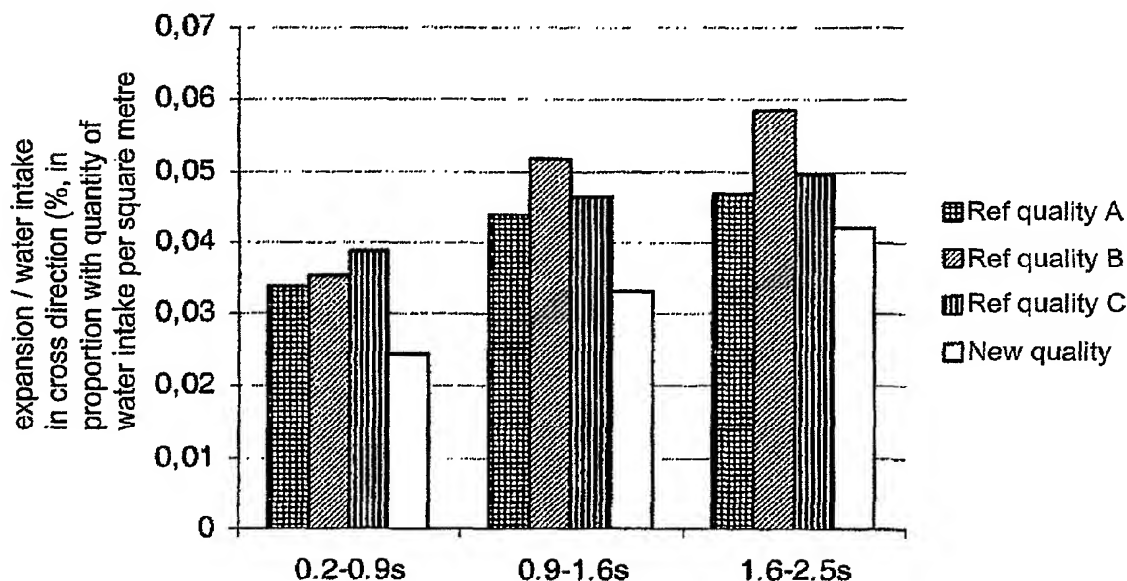
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(54) Title: SURFACE SIZED PAPER



(57) Abstract: The invention relates to a paper comprising a base paper and, on at least one side of the base paper, a surface size layer comprising an inorganic pigment and a polyvinyl alcohol (PVA). The surface size layer comprises an acrylic alkylene copolymer.

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### Surface sized paper

The present invention relates to a paper comprising a base paper and, on at least one side of the base paper, a surface size layer comprising inorganic pigment and polyvinyl alcohol (PVA).

The surface sizing of a glazing-type base paper with a surface sizing agent comprising an inorganic filler and polyvinyl alcohol, is known from prior art. The polyvinyl alcohol is a good film forming agent and is therefore commonly used in surface sizing agents. However, the properties of the surface sizing agents include deficiencies which must be compensated for by, for example, strong calendering treatments, to make the surface of the base paper as free from pores as possible before its siliconization. Furthermore, the surface sizing agents must be compatible with silicon in such a way that the silicon can adhere to and reticulate on the surface sizing agent.

The paper according to the invention is characterized in that the surface sizing layer comprises an acrylic alkylene copolymer and/or its derivatives.

When the surface sizing layer of the paper according to the invention comprises an acrylic alkylene copolymer and/or its derivatives, the surface energy of the surface sized paper can be adjusted to such a level that the siliconizability is improved. The improvement in the siliconizability means, among other things, lower silicon consumption, better results in Shirlastain colour tests, and lower release values of the siliconized paper. The addition of an acrylic alkylene copolymer to the surface sizing agent makes the surface of the surface-sized paper more hydrophobic, wherein the surface of the paper does not necessarily need to be treated to be completely poreless by calendering treatments.

The base paper used for the paper according to the invention can be a glazing-type paper or a kraft paper.

The glazing paper refers to a paper which is made of chemical pulp and whose grammage is typically from 50 to 150 g/m<sup>2</sup>. Good transparency is typically required of the glazing paper; for a 60 g/m<sup>2</sup> paper, it is typically at least 45, measured with visible light (ISO 2469:1994).

5 Because glazing paper is used as the base paper for release paper, a poreless surface is a requirement for good siliconizability. The poreless surface can be achieved with calendering treatments and surface sizing. The paper can be either calendered first and then surface sized, or surface sized first and then calendered. Preferably, the calendering is

10 performed first, wherein a calender with more than one nip is preferably used in the calendering. The calender can be a multi-nip calender or a supercalender. In the calender, at least one nip is formed between a hard-faced roll and a soft counter surface. To produce glazing paper, the moisture content of the paper is preferably at least 14 wt-% before

15 the calendering. Now that the surface sizing agent according to the invention is used, however, the calendering treatment is not as critical as before, because the hydrophobic property of the surface sizing agent can be used to compensate for the porosity left after the calendering treatment.

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The surface sizing agent according to the invention comprises at least an inorganic pigment and an adhesive. The adhesive comprises a polyvinyl alcohol and an acrylic alkylene copolymer, such as an acrylic ethylene copolymer, and/or its derivatives. The acrylic alkylene

25 copolymer and/or its derivatives mean that the acrylic alkylene copolymer is mixed, before mixing with the surface sizing agent, with an aqueous solution of a strong base, such as sodium hydroxide, and in this way a water-soluble salt is obtained from the acrylic alkylene copolymer. That is, the acrylic alkylene copolymer is first added into the

30 solution, and by the effect of the base, it is converted at least partly to the form of a water-soluble salt. The content of the acrylic alkylene copolymer is normally from 15 to 25 wt-% of the solution comprising water, a suitable base and said acrylic alkylene copolymer. The pH of the solution is from 8.5 to 9.5, preferably more than 9.

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The content of the adhesive is normally about 70 to 90 wt-% of the dry matter of the surface sizing agent. The adhesive comprises a polyvinyl alcohol and an acrylic alkylene copolymer and/or its derivatives. The content of the polyvinyl alcohol may be 30 to 40 wt-% of the dry matter of the surface sizing agent; the content of the acrylic alkylene copolymer may be 20 to 70 wt-%, preferably 20 to 50 wt-% of the dry matter of the surface sizing agent. Furthermore, the surface sizing agent may contain various additives, such as thickening agents. As an additive, it is possible to use, for example, carboxyl methyl cellulose (CMC), which improves water retention. The content of the additives is 0 to 2 wt-%, preferably not more than 1 wt-% of the dry matter of the surface sizing agent.

The inorganic agent may be an inorganic pigment known as such from papermaking, for example kaoline or talc. Mixtures of various inorganic pigments are also feasible. The content of the inorganic pigment as dry matter in the surface sizing agent is 20 to 70 wt-%, normally 20 to 30 wt-%.

The surface sizing is preferably performed with a film size press, and the surface sizing agent is then dried. After the surface sizing agent has been applied onto the surface of the base paper, the surface sizing agent may need to be neutralized to make the pH of the paper surface favourable for the subsequent silicon treatment. The surface sizing agent is neutralized to the level of pH 7 by using a suitable pH lowering agent. Thus, the water-soluble salt of the acrylic alkylene copolymer is changed, at least partly, back to a water-insoluble form.

In the following, the invention will be described with reference to the examples and the figure. The figure shows graphically the transverse expansion / water intake of a paper which has been surface sized by the formulation according to Example 1, and reference samples of prior art. The results in the figure show that the paper according to the invention expands less than the reference samples.

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## Example 1.

A glazing-type base paper was surface sized by using, as the surface sizing agent, a composition containing 34.5 % of polyvinyl alcohol, 34.5 % of acrylic ethylene copolymer, 30 % of kaoline, and 1 % of carboxymethyl cellulose, calculated as weight per cent of the dry matter. The acrylic ethylene copolymer was present in a solution of sodium hydroxide mixed with 20 wt-% of acrylic ethylene copolymer. In the sodium hydroxide solution, the acrylic ethylene copolymer is changed into a water-soluble sodium salt. The content of ethylene in the copolymer was 80 wt-%. The pH value of the solution was approximately 9.

The surface-sized and dried paper according to the invention was analyzed for its properties, and the results were compared with a paper of prior art. The results are shown in Table 1.

Table 1. Test results of the surface-sized paper.

Property	Measured	Unit	Paper according to the invention	Paper of prior art
<b>Thickness</b>	average	µm	56,2	57,0
	standard deviation	"	1,2	1,3
Porosity (Bekk)		s	464	158
Oil absorption (Unger 60 s)	surface	g/m <sup>2</sup>	0,69	0,70
Shirlastain 60 s 50 %	surface	g/m <sup>2</sup>	15,9	19,0
	back	"		25,9
Cobb 60 s	surface	g/m <sup>2</sup>	13	17,3
Bekk smoothness	surface	s	3564	1266
	back	s	265	808
Gloss (Hunter 75°)	surface	%	57,6	59,5
	back	%	36,8	48,7
<b>PPS-10 roughness</b>	surface	µm	1,3	not measured
	back	µm	2,7	not measured

The values given in the table were measured according to the following standards:

	Thickness	SCAN-P 7:75
5	Bekk porosity	ISO 5627
	Oil absorption (Unger)	SCAN-P 37:77
	Shirlastain	as Cobb, but with Shirlastain liquid
	Cobb	ISO 535
10	Bekk smoothness	DIN 53107
	Gloss	TAPPI T480 OS-78
	Roughness (PPS)	SCAN-P 76:95

The results show that the Cobb value, which indicates the hydrophobicity of the paper, is clearly lower for the paper according to the invention than for the paper of prior art. From the Cobb values, it can be stated that values exceeding  $17 \text{ g/m}^2$  are common at present, and values which are not higher than  $\text{g/m}^2$  are good. For the paper of the invention, the Cobb value is typically not higher than  $17 \text{ g/m}^2$ , advantageously not higher than  $16 \text{ g/m}^2$ , and preferably not higher than  $15 \text{ g/m}^2$ .

Furthermore, the results show that the Shirlastain value for the surface-sized side is lower than  $18 \text{ g/m}^2$ . When the Shirlastain value is not higher than  $18 \text{ g/m}^2$ , the value is considered good.

The above description does not restrict the invention, but the invention may vary within the scope of the claims.

Claims:

1. A paper comprising a base paper and, on at least one side of the base paper, a surface sizing layer which contains inorganic pigment and polyvinyl alcohol (PVA), **characterized** in that the surface sizing layer comprises an acrylic alkylene copolymer and/or its derivatives.  
5
2. The paper according to claim 1, **characterized** in that the comonomer of the acrylic alkylene copolymer is ethylene.  
10
3. The paper according to claim 1 or 2, **characterized** in that the inorganic filler is kaoline, talc, or a mixture of these.
4. The paper according to any of the preceding claims, **characterized** in that the surface sizing layer comprises carboxymethyl cellulose (CMC).  
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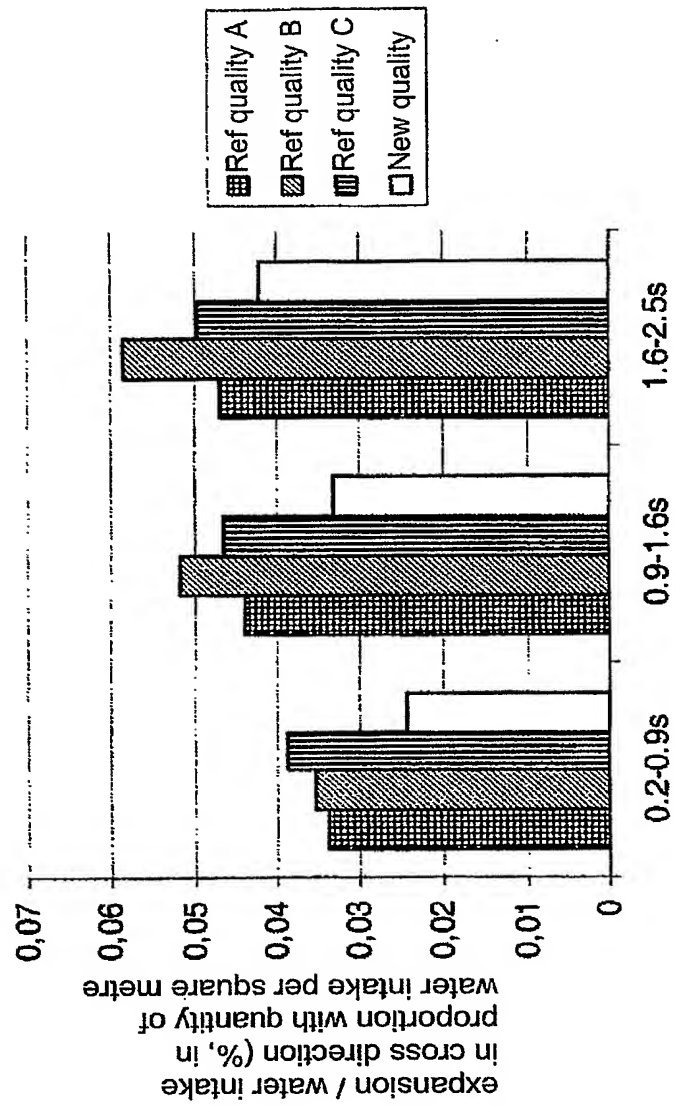


Fig.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2004/000329

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21H 17/34, D21H 19/56, D21H 21/16, D21H 27/06 // D21H 17/36, D21H 17/37  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3674896 A (CHESTER L. PURCELL ET AL), 4 July 1972 (04.07.1972), column 2, line 6 - line 49; column 3, line 68 - line 71; column 11, line 52 - column 12, line 69, claims 1-3	1-3
Y	--	4
X	WO 0117774 A1 (TETRA LAVAL HOLDINGS & FINANCE S A), 15 March 2001 (15.03.2001), page 5, line 31 - page 6, line 12, claims 1-10	1-3
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance  
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 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 0155507 A1 (UPM-KYMMENE CORPORATION), 2 August 2001 (02.08.2001), page 2, line 13 - line 32, claims 1-15	1-3
Y	--	4
A	EP 1279768 A2 (RICOH COMPANY, LTD.), 29 January 2003 (29.01.2003), claims 1-8	1-4
A	--	
A	US 6426120 B1 (ROBERT STOCQ ET AL), 30 July 2002 (30.07.2002), column 2, line 8 - column 3, line 5, abstract	1-4
A	--	
A	US 5807781 A (BERND REINHARDT ET AL), 15 Sept 1998 (15.09.1998), claims 1-4	1-4
	-- -----	

## INTERNATIONAL SEARCH REPORT

Information on patent family members

03/09/2004

International application No.

PCT/FI 2004/000329

US	3674896	A	04/07/1972	AT	296459	B	10/02/1972
				AU	447937	B	17/04/1974
				AU	4976069	A	19/11/1970
				BE	702016	A	29/01/1968
				BR	6791547	D	00/00/0000
				CH	208368	D	15/11/1971
				CH	485827	A	15/02/1970
				CH	520226	A	15/03/1972
				DE	1646160	A	08/07/1971
				FI	53334	B,C	30/12/1977
				FR	1532958	A	12/07/1968
				GB	1201811	A	12/08/1970
				NL	6710476	A	29/01/1968
-----							
WO	0117774	A1	15/03/2001	AU	7326300	A	10/04/2001
				BR	0013797	A	14/05/2002
				CN	1387479	T	25/12/2002
				EP	1237721	A	11/09/2002
				JP	2003508274	T	04/03/2003
				SE	516918	C	19/03/2002
				SE	9903176	A	08/03/2001
-----							
WO	0155507	A1	02/08/2001	FI	20000151	A,V	27/07/2001
-----							
EP	1279768	A2	29/01/2003	JP	2003147696	A	21/05/2003
				US	6670010	B	30/12/2003
				US	20030031820	A	13/02/2003
-----							
US	6426120	B1	30/07/2002	AU	5798700	A	30/01/2001
				BE	1013060	A	07/08/2001
				EP	1119660	A	01/08/2001
				WO	0104418	A	18/01/2001
-----							
US	5807781	A	15/09/1998	DE	4425737	A,C	01/02/1996
				EP	0697484	A	21/02/1996
				FI	953486	A	22/01/1996
				JP	2683718	B	03/12/1997
				JP	8188992	A	23/07/1996
-----							